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In the study reported here the techniques of LEED and angle- and energy-resolved photoemission have been used to investigate some of the properties of CO/Co(0001). The orientation of the CO molecules was determined using well-established symmetry selection rules. The CO-CO direct interaction was measured by mapping out the E vs. $k_{\parallel}$ dispersion of the 4σ and combined $5\sigma/1\pi$ levels of CO in several directions in the Surface Brillouin Zone (SBZ) at two coverages of CO, corresponding to the saturated room and low (170°K)

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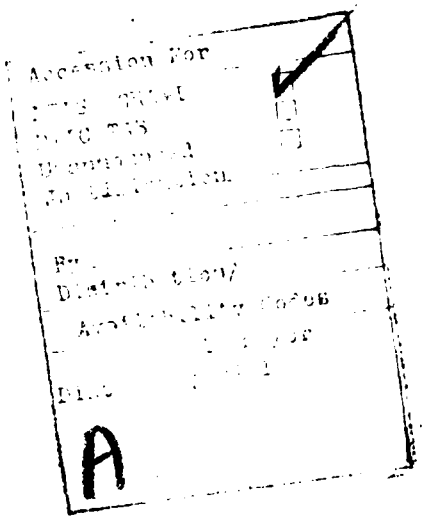
20. Abstract (continued)

temperature phases. The dispersion can be related to the size and shape of the SBZ and correspondingly to the geometry of the CO overlayer in real space.

After preliminary LEED work, a photoemission study was performed at the Synchrotron Radiation Lab of the University of Wisconsin. Two distinct peaks were seen in the UPS spectra of CO/Co(0001) with p-polarization of the incident light, as is generally observed on other transition metals. The consensus is that the level with the higher binding energy (at ~11 eV) corresponds to the 4σ level of the isolated CO molecule, while the level at ~8 eV is a superposition of the molecular 5σ and 1π levels, with the 5σ level having undergone a bonding shift of ~3 eV with respect to the free molecule.



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Angle-Resolved Photoemission Study of CO/Co (0001)

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D. Heskett, F. Greuter, H.-J. Freund, and E. W. Plummer

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Abstract

Angle-Resolved Photoemission Study of CO/Co(0001)

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In the study reported here the techniques of LEED and angle- and energy-resolved photoemission have been used to investigate some of the properties of CO/Co(0001). The orientation of the CO molecules was determined using well-established symmetry selection rules. The CO-CO direct interaction was measured by mapping out the E vs. $k_{\parallel}$ dispersion of the 4σ and combined 5σ/1π levels of CO in several directions in the Surface Brillouin Zone (SBZ) at two coverages of CO, corresponding to the saturated room and low ($170^{\circ}K$) temperature phases. The dispersion can be related to the size and shape of the SBZ and correspondingly to the geometry of the CO overlayer in real space.

After preliminary LEED work, a photoemission study was performed at the Synchrotron Radiation Lab of the University of Wisconsin. Two distinct peaks were seen in the UPS spectra of CO/Co(0001) with p-polarization of the incident light, as is generally observed on other transition metals. The consensus[3] is that the level with the higher binding energy (at ∿ 11 eV) corresponds to the 4σ level of the isolated CO molecule, while the level at ∿ 8 eV is a superposition of the molecular 5σ and 1π levels, with the 5σ level having undergone a bonding shift of ∿ 3 eV with respect to the free molecule.

We determined the orientation of the CO molecules in the room temperature phase of CO/Co(0001) by making use of the polarized nature of the radiation from the synchrotron. The almost complete disappearance of the 4σ level (and presumably the 5σ as well) in the so-called "forbidden" geometry indicates that the molecular axis is preferentially aligned to the surface normal[4]. This is in agreement with the general picture of CO bonding to metals[5]. Further support for this picture comes from observation of resonances in the cross sections of the 4σ and 5σ/1π levels versus photon energy for p-polarized light.[6] The cross sections peak along the surface normal and decrease significantly on going off normal.

The dispersion of the 4σ and the 5σ/1π levels was measured in two directions in the SBZ for both phases of CO/Co(0001). The 5σ and 1π levels are not expected to disperse together; however, in the results presented here, we were unable to resolve two distinct peaks in the room temperature phase, although the peak width was observed to change.

The extended SBZ for the $\sqrt{3} \times \sqrt{3}$ R30°, corresponding to the room temperature phase as seen in LEED, is given in Figure 1. The coverage for this structure is $\theta = 1/3$ and the CO nearest neighbor spacing is 4.35 Å. The dispersion was measured along the $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ and the $\bar{\Gamma}$-$\bar{K}$-$\bar{M}$ directions. The results are presented in Figure 2. There are several observations to be made about these results: 1. The shapes of the 4σ and 5σ/1π dispersions are quite similar, indicating that the 5σ peak dominates the 5σ/1π dispersion at the photon energies used. The qualitative behavior of these levels is as expected since σ levels are bonding with respect to the CO-CO interaction and should have a minimum at the $\bar{\Gamma}$ point, dispersing upwards from there, as seen. On the other hand, π levels are anti-bonding and will disperse down-

ward from Γ. 2. The magnitude of the 5σ dispersion is greater than that of the 4σ level. This can be explained by the greater spatial extent of the 5σ (and also the 1π) level vs. the 4σ in real space[6,7]. More overlap of the 5σ orbitals should result in a larger bandwidth. 3. In the Γ-M-Γ direction in the SBZ, the 4σ dispersion is approximately symmetric about the M point and drops back to its original value as Γ is approached in the 2nd SBZ. This periodicity is in agreement with the $\sqrt{3} \times \sqrt{3}$ R30° observed with LEED. 4. The 5σ/1π level does not appear to have the same symmetry about the M point. An explanation for this is increased emission of the 1π level for large collection angles[3], corresponding to large values of $k_{||}$.

At low temperatures the room temperature phase can be compressed; the dispersion results for this low temperature phase are given in Figure 3. Shown are zone body crossings for the $2\sqrt{3} \times 2\sqrt{3}$ R30° structure proposed by Papp[8] (corresponding to θ = .58 and a CO spacing of 3.32 Å at 100°K). Important features are the following: 1. The magnitude of the dispersion for both levels is larger than the corresponding bandwidths in the room temperature phase. This is consistent with the picture of increased interaction with higher coverage resulting from more orbital overlap as the nearest neighbor distance decreases. 2. The periodicity in $k_{||}$ space is larger in the low T phase. This is expected as with higher coverage the real space lattice is more compressed, yielding larger zones in reciprocal space. 3. The shape of the dispersion is the same for both levels in both directions: symmetric about $k_{||} = 1.2$ Å^{-1}. This $k_{||}$ is close to the zone boundary crossings in two orthogonal directions for the proposed $2\sqrt{3} \times 2\sqrt{3}$ R30° lattice, as indicated in Figures 1 and 3. The fact that the dispersions of the levels does not drop back down to the original values at Γ is due to the fact that the directions probed in the SBZ of the $2\sqrt{3}$ structure are low symmetry directions and Γ will not be reached in another zone except for very large

values of $k_{||}$. The measured dispersion is also qualitatively consistent with other high coverage overlayer geometries (such as a c(4x2) or ($\sqrt{7}/2$ x $\sqrt{7}/2$) R19.1°) but not with lower coverage phases (i.e., $\theta \leq .5$).

The above dispersion results can be understood qualitatively by considering the symmetry properties of an isolated CO layer. A measure of the strength of the CO-CO interaction is obtained by noting that a 24% reduction in CO spacing in going to the low temperature phase corresponds to a factor of 2 2/3 to 3 increase in the dispersion.

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Acknowledgements

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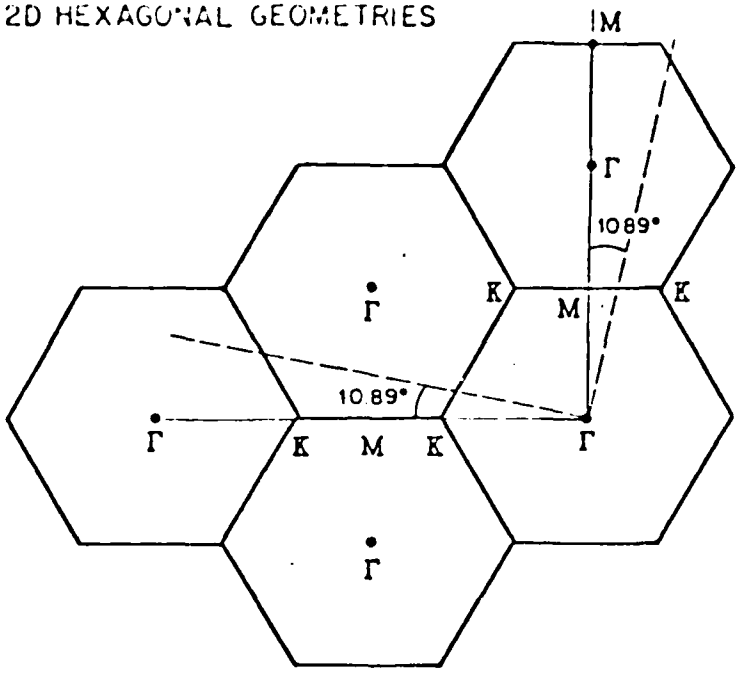
EXTENDED SURFACE BRILLOUIN ZONE
FOR 2D HEXAGONAL GEOMETRIES



SOLID LINE
Direction in overlayer SBZ probed in $(\sqrt{3} \times \sqrt{3})$ R 30° phase.

DASHED LINE
Direction probed for $(2\sqrt{3} \times 2\sqrt{3})$ R 30° structure.

Fig. 1

Fig. 2

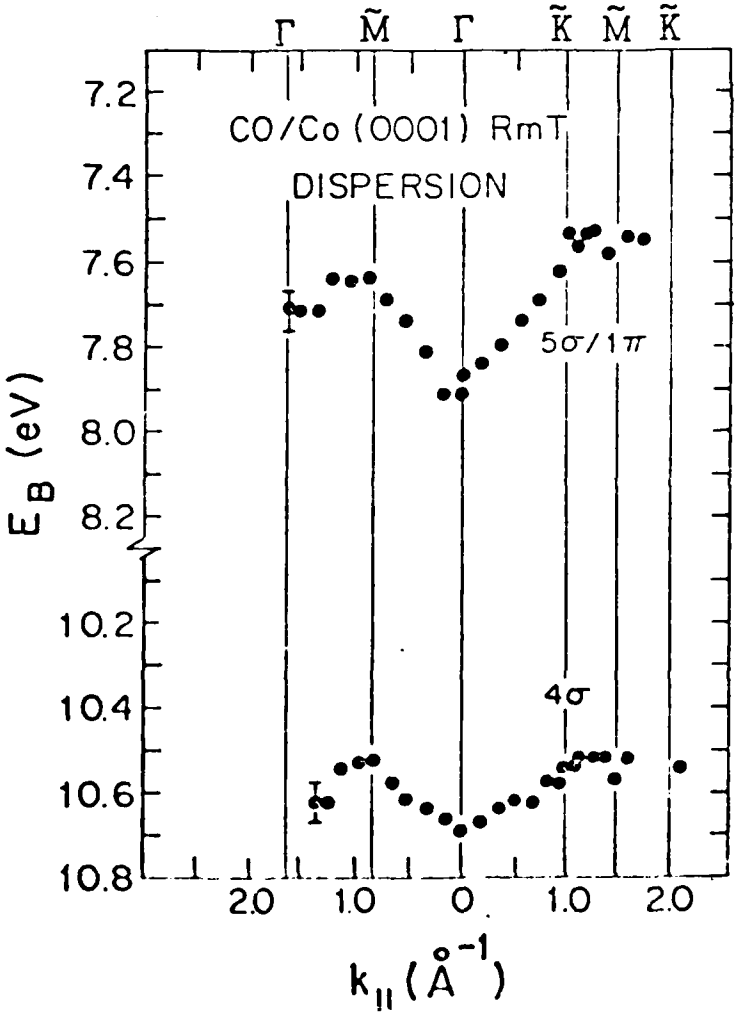
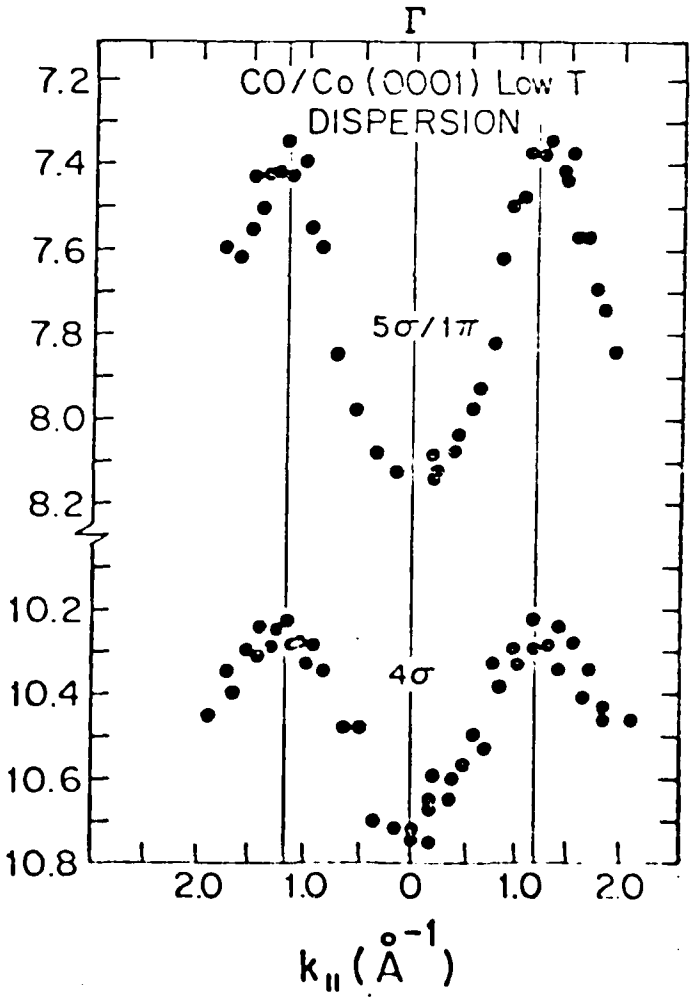



Fig.3